

Supplementary Information

Poly(divinylbenzene) as fiber coating for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons from river water

Mengyuan Li,^a Xitong Ren,^b Yanmei Gao,^a Mengyao Mu,^a Shiping Zhu,^a Dan Li,^a Shufang Tian,^{*a} Peige Qin^a and Minghua Lu^{*a}

^a College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, Henan, China.

^b Key Laboratory for Special Functional Materials of Ministry of Education, School of Materials Science and Engineering, Henan University, Kaifeng 475004, China

Corresponding Authors

*Phone: (+86) 371-23881589. Fax: (+86) 371-23881589. E-mail: tianshufang@henu.edu.cn (S. Tian); mhlu@henu.edu.cn (M. Lu)

1 Materials and methods

1.1 Reagents and standards

Naphthalene (NAP), acenaphthene (ANE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), pyrene (PYR), toluene, acetonitrile, acetone, THF, polyimide sealing resin were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Divinylbenzene (DVB80, 80% divinylbenzene isomers) was purchased from J&K Chemical (Shanghai, China). 2, 2'-Azobisisobutyronitrile (AIBN) was received from Shisihewei Chemical Co., Ltd (Shanghai, China). The fibers (stainless-steel wires) were supplied by Hengwang Metal Material Factory (Guangzhou, China). Acetone (HPLC grade) was purchased from Merck KGaA (Darmstadt, Germany). The ultrapure water purified by Milli-Q purification system (Millipore, Bedford, MA, USA) was used in all the experiments. Acetonitrile was dried over 4 Å molecular sieves and purified by distillation prior to use. Other reagents used in experiments were analytical grade without further purification.

1.2 Instruments

All gas chromatographic analyses were performed on an Agilent 7890B GC (Agilent, China) equipped with an FID detector. A HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) was used in all the experiments. Parameter settings are based on literature³ with some modifications. The column temperature program was 60 °C held for 1 min. Next increased with 48.5 °C/min to 190 °C and held for 1 min. Then increased to 220 °C by 6 °C/min and held for 0.5 min. Finally, the oven temperature was arrived at 300 °C with a rate of 80 °C/min and kept for 2 min. The detector temperature was set at 300 °C. In splitless mode, high purity nitrogen (99.99%) with constant flowrate of 1 mL/min was used as the carrier gas in all cases.

The morphology of the poly(divinylbenzene) microspheres was characterized by

scanning electron microscopy (SEM, JEOL JSM-7610F Plus, Japan). The types of chemical bonds and functional groups were recorded with VERTEX 70 (Bruker, Germany) infrared spectrometer. X-ray powder diffraction (XRD) pattern were acquired by X-ray diffractometer equipped with a Bruker D8 Advance (Bruker-AXS, Germany). Thermal stability evaluation was performed on thermogravimetric (TG) analyzer (QMS 403 D Aëolos®, NETZSCH, Germany). The hydrophilicity and hydrophobicity of materials were judged by contact angle tester (KRÜSS DSA25, Germany). Nitrogen adsorption analysis was conducted on gas adsorption instrument (Quadrasorb SI-4, USA). The IKA magnetic stirrer (Germany) was used for stirring the sample and SB-120 DT ultrasonicator was obtained from Ningbo Scientz Biotechnology (China).

1.3 Preparation of porous poly(divinylbenzene) microspheres

Porous PDVB microspheres was synthesized according to the distillation precipitation polymerization method of Bai.¹ In brief, 0.046 g AIBN and 2.5 mL DVB were dissolved in 75 mL of acetonitrile and 25 mL of toluene mixture in a flask. The reaction mixture heated to boiling within 30 minutes. Then the co-solvent was distilled from the reaction system. The reaction ended when 50 mL of co-solvent distilled off. After cooling to ambient temperature, the product was separated by suction filtration and washed three times with THF and acetone. Finally, the obtained products were dried overnight at 60 °C to get porous polymer microspheres.

1.4 Preparation of porous PDVB coated fiber

Stainless steel wire was used as support for the preparation of PDVB-coated fiber. One end of a 5 cm long stainless steel wire was immersed in aqua regia solution for 80 seconds to obtain a rougher surface. The porous PDVB was bonded to the fiber with polyimide sealing resin. After that, the fiber was installed into a 5 µL micro-syringe

purchased from Goger (Shanghai, China) to form a SPME device, and then exposed in the GC inlet at 300 °C for 1 h to avoid any contamination.

1.5 HS-SPME procedures

Sample solution was introduced into 50 mL glass vial with PTFE-coated septa. The PDVB-coated fiber was exposed to the headspace with a height of about 0.5 cm from the surface of sample solution. Distribution of target analytes between coating and sample by controlling water bath temperature, adsorption time and magnetic stirrer speed. After equilibration, the fiber was taken out and inserted into the gas injection port to thermally desorb the substances adsorbed on the fiber.

1.6 Sample preparation

The PAHs stock solution was prepared by dissolving PAHs respectively in acetone to a concentration of 1 mg mL⁻¹. The 100 µg mL⁻¹ mixed PAHs stock solution was diluted from single PAHs stock solutions. The PAHs working standard solution of 2 µg mL⁻¹ was obtained by diluting the mixed PAHs stock solution. All solution was kept at 4 °C refrigerator prior to use. Water sample was collected from Jianshui River in Kaifeng. Water sample was filtered with an aqueous filter (0.45 µm) prior to analysis. All sample measurements are the average of three replicate measurements.

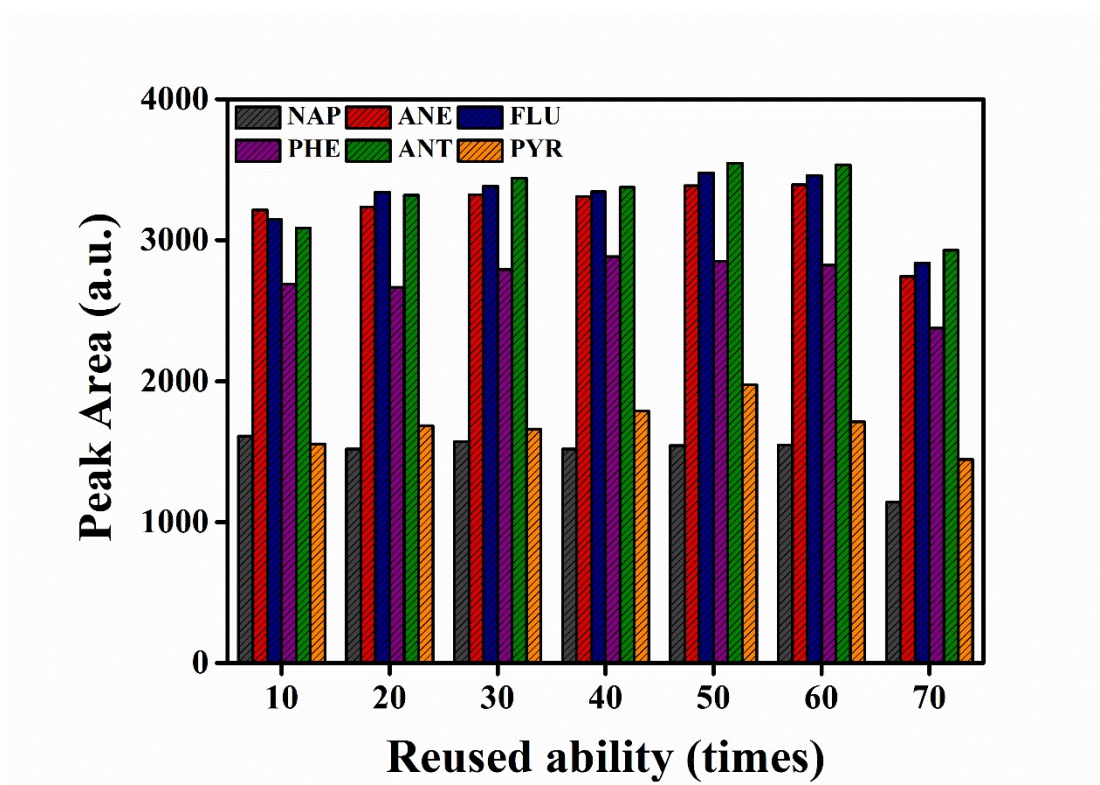
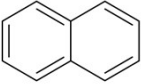
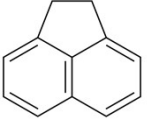
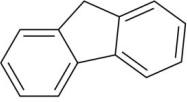
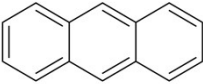

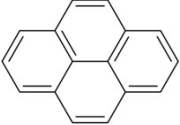


Fig. S1 The reused ability of mesoporous PDVD coated SPME fiber for extraction of PAHs.

Table S1 Chemical structure and hydrophobic constant of PAHs which were selected as targets.

Analytes	Chemical structure	Molecular weight	$\log K_{ow}^a$
NAP		128.171	3.30
ANE		154.208	3.92
FLU		166.219	4.18
PHE		178.229	4.46
ANT		178.229	4.45
PYR		202.251	4.88

^a $\log K_{ow}$: n-octanol/water partition coefficients, indicator for hydrophobicity. Data taken from RSC publishing Home: <http://www.chemspider.com/>

Table S2 The linear range, linear equation, correlation coefficient (r), limit of quantification (LOQ), limit of detection (LOD), enrichment factor (EF) and relative standard deviation (RSD) of the HS-SPME using mesoporous PDVB as fiber coating for the analysis of PAHs.

Analytes	Linear range (ng mL ⁻¹)	Linear equation	r	LOQs (ng mL ⁻¹)	LODs (ng mL ⁻¹)	EFs	RSDs(%)		
							intraday (n=5)	interday (n=5)	fiber-to-fiber (n=3)
NAP	0.02-50	$y = 74.02x - 1.220$	0.9996	0.02	0.006	5963	8.42	11.4	7.92
ANE	0.01-50	$y = 164.6x + 14.96$	0.9999	0.01	0.003	8614	3.23	3.96	2.37
FLU	0.01-50	$y = 159.7x + 50.37$	0.9995	0.01	0.003	9963	3.42	5.78	2.42
PHE	0.02-50	$y = 141.8x - 2.412$	0.9999	0.02	0.004	16720	3.57	2.61	3.06
ANT	0.01-50	$y = 157.1x + 64.16$	0.9988	0.01	0.003	8381	2.61	3.97	2.79
PYR	0.02-50	$y = 92.35x + 1.027$	0.9996	0.02	0.006	8384	8.99	12.3	11.4

Table S3 The comparisons with other materials as SPME fiber coating for the analysis of PAHs.

Coating materials	Extraction and analytical methods	Linear range (ng mL ⁻¹)	Thermal stability	LODs (ng mL ⁻¹)	EFs	Refs
GOCS aerogel	DI-SPME-GC-MS	0.0005-1	280	0.00003-0.00128	311-3740	2
Polyacrilate	DI-SPME-GC-HRMS	0.001-1.5	N. P. ^a	0.00005-0.005 (LOQs)	79-1356	3
SMASNS	DI-SPME-GC-MS	0.01-10	500	0.00014-0.00024	N. P.	4
Etched stainless steel wire	HS-SPME-GC-FID	2.5-50	N. P.	0.24-0.63	2541-3981	5
Peanut shell-derived biochar	HS-SPME-GC-MS	0.01-20	N. P.	0.0011-0.0025	N. P.	6
TAPB-TMC-COF	HS-SPME-GC-MS	0.0002-2	N. P.	0.0003-0.0009	819-2420	7
CIM-80(Al)	HS-SPME-GC-MS	0.005-0.5	400	0.0005-0.0015	N. P.	8
Mesoporous PDVB	HS-SPME-GC-FID	0.01-50	420	0.003-0.006	5963-16720	This work

^a Not provided

Table S4 The contents of PAHs in river water and recoveries of the developed method.

Analytes	Detected (ng mL ⁻¹)	Added (ng mL ⁻¹)	Recovery (%)	RSDs (%; n=3)
NAP	Not found	0.20	91.65	3.62
		1.00	96.52	3.66
		20.00	96.54	8.25
ANE	0.15	0.20	96.56	3.04
		1.00	99.21	1.65
		20.00	89.04	3.68
FLU	0.06	0.20	93.29	5.32
		1.00	101.11	3.37
		20.00	97.63	4.78
PHE	Not found	0.20	86.06	4.22
		1.00	98.87	8.93
		20.00	90.71	6.04
ANT	Not found	0.20	91.44	5.43
		1.00	105.81	2.08
		20.00	99.02	5.77
PYR	Not found	0.20	94.80	3.68
		1.00	118.85	1.20
		20.00	93.89	5.17

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